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Multiphoton Processing of Composite Materials and Functionalization of 3D Structures

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9.1

Overview

Three-dimensional (3D) multiphoton lithography (MPL) is highly appealing as a fabrication and manufacturing technology because it provides a means for creating previously inaccessible structures that can have transformative applications in optics, sensing, imaging, consumer electronics, microelectromechanical systems (MEMS), and medicine. Yet most applications require not only well-defined 3D forms but also functional properties that are manifest in controlled chemical, mechanical, optical, electronic, or thermal interactions with the environment. Indeed, for many micro-/nanodevices, the overall performance depends sensitively upon the synergistic combination of small-scale form and properties. A good example is meta-structured materials, such as photonic crystals (PCs), for which the optical function is derived from the combination of sub-wavelength-scale structure as well as the bulk optical properties of the constituent material itself [1]. Microfluidics provide another good example, as these can be engineered to have peculiar and useful flow and mixing characteristics that derive from the combination of the channel size, shape, and cross-section with the chemical nature at the interface formed by the microfluidic walls and the fluid [2, 3].

The laser-induced change most commonly leveraged for MPL is photo-induced polymerization or cross-linking of an organic monomer or oligomer. Creating 3D micro-/nanoscale polymeric structures by MPL continues to serve many purposes, but a growing number of current applications require a wider range of materials to achieve targeted functions. In a limited number of situations, it has been possible to identify alternative materials that can be patterned in much the same way as a photopolymer. For example, thermally deposited arsenic sulfide [4] and other chalcogenides [5] can be directly photocrosslinked and then chemically etched, behaving like an inorganic analog of a photoresist that can be used to directly create functional 3D semiconductor nanostructures. But such materials are by far the exception, and in most cases it has been necessary to engineer

new materials and processes for MPL that provide access to the wider range of properties and functions needed for a given application.

The imperative to create functional micro-/nanoscale structures has led many investigators to develop complementary approaches for multiphoton processing of composite materials and functionalization of 3D structures. The approaches that have been reported for integrating specific properties or function into 3D microstructures can be divided into three classes, as illustrated in Figure 9.1: (i) MPL using composites, (ii) post-MPL functionalization, and (iii) templated deposition or back-filling.

In the first approach (Figure 9.1b), a composite material [6] is formulated that is both suitable for direct fabrication of the targeted microscale form by MPL and contains one or more additives that endow the final microstructure with the targeted functionality. Such composites are typically formulated so that a large fraction of the total mass is comprised of a polymerizable monomer and/or oligomer and a multiphoton-activatable initiator that are known to be suitable for MPL. A wide range of functional structures can be accessed by this approach. For example, optically functional microstructures can readily be created by blending a molecular chromophore into a polymeric MPL medium [7]. Composites

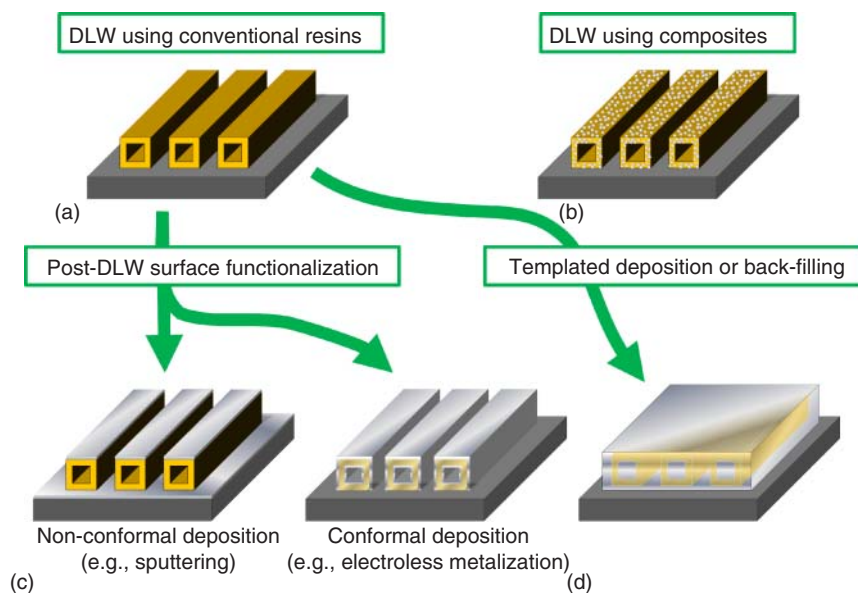


Figure 9.1 Schematic illustrating the general approaches that have been used to create functional microstructures by MPL in a wide range of materials. Rather than (a) fabricating 3D microstructures using a conventional photopolymer, (b) a composite can be engineered and used to fabricate structures with

targeted properties or function. Alternatively, (c) a structure created by MPL using a conventional (or subtly modified) photopolymer can be functionalized after fabrication by chemical or physical deposition, or (d) used as a template for direct deposition of a second material onto the targeted form.

containing photo-reducible metal salts and/or metal nanoparticles have been formulated and used to create electrically conductive structures by MPL [8, 9]. The composite approach has the advantage that the functional structure can be fabricated in a single MPL step. But it has the disadvantage that the additives must be present at low weight loading so as to not interfere with the multiphoton excitation and polymerization processes.

In post-MPL functionalization (Figure 9.1c), a conventional MPL medium is used to create the targeted 3D form, and post-fabrication chemistry or physical deposition processes are used to deposit a second material onto the 3D form. Conformal and nonconformal deposition approaches can be selected as needed for the targeted application. Deposition approaches such as sputtering and physical vapor deposition tend to be nonconformal, depositing material primarily on those surfaces of the 3D structure that are exposed by “line of sight” to the source [10, 11]. Conformal deposition, in which all surfaces of the 3D microstructure are coated uniformly, can be achieved using a variety of approaches. Chemical-bath-based methods, such as electroless deposition [12, 13], can be used to deposit conductive metal conformally onto the 3D form. Other approaches, such as chemical vapor deposition (CVD) [14] and atomic layer deposition (ALD) [15] have also been used for conformal deposition. In some cases, the MPL medium may be modified slightly by incorporating an additive that makes the 3D structure active toward subsequent surface functionalization [16–19]. For polymeric media, unreacted functional groups at the surface can be sufficiently active so that surface functionalization can be carried out without the need to add additional components to the MPL medium [13, 20]. The post-MPL functionalization approach has the advantage that it decouples fabrication of the 3D structure from deposition of a targeted material, which eliminates potential complications that can arise in attempting to create a composite. A major disadvantage is that the functional material is usually present only on the outside of the structure, and not throughout the bulk of the 3D form, which can compromise performance. An example might be an electronic function, where the deposition of a thin skin of conductive metal would have much lower conductivity than an idealized bulk-metal structure, or one that could potentially be created by a composite approach. Bulk functionalization can occur when a surface functionalization agent is able to diffuse into the bulk of the crosslinked polymeric structure [20, 21].

With templated deposition, or backfilling (Figure 9.1d), MPL in a conventional photopolymer blend is used to create a free-standing 3D form upon which a second material is deposited to completely (or nearly completely) fill the void space between features of the 3D structure. This might be viewed as an extreme limit of post-MPL functionalization, where the deposition is simply continued until a maximally thick layer is deposited. The back-filled medium is the structural inverse of the original template. This has been achieved by ALD of silica [22] and by galvanic deposition of metal around a structure fabricated on a conductive surface [23]. The functional device could consist of the infiltrated template, or the final device could be obtained after using plasma etching or other approaches to remove the polymeric template, leaving the inverted structure in the second

material. A second round of infiltration in another material can be used to re-invert the structure back to its original form in the final material. This approach was demonstrated by depositing silicon onto a silicate inverted structure as a means for preparing 3D silicon PCs [22]. Overall, templated deposition also offers the advantage that 3D patterning and targeted material deposition are decoupled, enabling both processes to be separately optimized, and it provides a means for creating bulk 3D structures from the second material. The primary disadvantage remains, again, that multiple fabrication steps are needed to produce the final structure, including alternate substrate bonding/removal steps.

Some methods for fabricating 3D micro/nanostructures in novel materials have employed processes that are essentially a combination of both the composite and surface functionalization approaches. For example, Kawata and coworkers reported a route to high-refractive-index PCs based on a polymeric “woodpile” lattice loaded with CdS nanoparticles [21]. The approach involved first patterning the woodpile lattice by MPL using a composite of a photopolymer doped with Cd^{2+} salts. After MPL, the woodpile structure was functionalized by exposing it to an atmosphere of H_2S . Molecules of H_2S diffused into the interstitial voids of the woodpile lattice as well as into the polymeric rods themselves, forming CdS nanocrystals throughout the structure. The resulting CdS-doped PC exhibited properties substantially different from those of a nonfunctionalized lattice.

Fabrication using composites, surface functionalization, or backfilling introduces a plethora of challenges. In addition to the general advantages and disadvantages listed above, the materials involved must be compatible with previous and subsequent steps, else the material function and 3D form can be compromised. Particular attention must be paid to chemical reactivity, solubility, swellability, and thermal tolerances associated with the materials and processing steps, as well as how these can disrupt the function or 3D form of the structure [20]. Adhesion and material compatibility are particularly important for interfaces created by surface functionalization or secondary deposition. Properties of the 3D form can also significantly affect those of the overall structure. For example, if the MPL patterning and processing creates features with high surface roughness, then a second material deposited onto the polymeric template could have desirable properties, such as high adhesion, as well as undesirable properties, such as high optical scattering. So invariably, fabrication involving multistep processing requires careful co-optimization of the processing conditions to achieve good performance from the 3D microstructure. It should also be noted that composite and surface functionalization can be used to create structures with either a passive or an active function. An actively functional device can be thought of as one that changes its form or physical properties in response to an environmental stimulus. These types of interactions often result from the combination of material, shape, or size of the device. One early example in the field of MPL involves a hydrogel composite that was formulated to respond to UV radiation, such that the structure underwent reversible mechanical deformation when exposed [24]. A wide range of applications can be effected by active-response devices, and their

advancement depends heavily on the progress in composite development and microstructure functionalization.

Over the past decade, many examples of the fabrication strategies described above have been reported. Each of these has substantially extended the technological impact of MPL by opening new routes to functional 3D micro/nanoscale structures that can have tailored function for a given application. Several reviews of MPL and extensions of the method have been published over the past decade [25–40], providing a wealth of information concerning methods for fabricating functional micro/nanoscale devices using a range of materials. The remainder of this chapter reviews methods for fabricating and functionalizing composite structures in terms of the material classes, rather than processing method, as applications are typically dependent upon the class of material needed for a targeted function, and the means by which it is deposited are a secondary concern.

9.2

Polymer–Organic Composites

Most commonly, MPL is performed using an organic composite, which is a homogeneous mixture of two molecular species: (i) a photoinitiator, responsible for multiphoton excitation, and (ii) a monomer, responsible for forming a polymer chain or crosslinked polymeric matrix, where the polymerization reaction is activated by the excited photoinitiator. Combinations of monomers have been used to improve specific properties, such as increasing the structure hardness or stability, or reducing shrinkage that can occur during polymerization or post-MPL processing [41]. Using higher performance materials avoids the need to add supports or solid frames that can compensate for anticipated shrinkage or distortion, but alters the overall structural form [42]. Using composites also provides a means for enhancing different material, optical, and chemical properties. Monomers such as acrylates [43] and epoxides [44] have been used interchangeably or in combination to fabricate different components and devices. However, most of these compositional changes yield passive devices that are limited in properties and use. To enhance the properties of fabricated structures or to create active devices, additional components have been incorporated, such as fluorescent dyes, optically active chromophores, and electrically active species.

9.2.1

Fluorescent-Dye-Doped Organic Microstructures

Fluorescent 3D organic microstructures have been realized via MPL using acrylate composites doped with fluorescent dyes and through post-fabrication chemical functionalization [18, 41]. Doping with a fluorescent dye yields active structures that can be used for sensing, photonics, or biomedical functions [45, 46]. A microstructure created with a polymeric composite containing rhodamine 610 at 0.5 wt% exhibited red fluorescence upon one- and two-photon

excitation at wavelengths of $\lambda = 480$ and 780 nm, respectively [47]. Incorporating rhodamine did not adversely affect the fabrication process, as the structure displayed good structural integrity and resolution. Optically active microstructures containing the conductive and luminescent polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) were observed to retain the fluorescence spectra of the dye after structure fabrication [41]. Complex 3D active microstructures were fabricated in acrylate resins mixed with the laser dye LD490 [48]. Two-photon confocal fluorescence showed that the microstructures were uniformly stained with the dye.

Microstructures that have a broad and tunable fluorescence emission from approximately $\lambda = 350$ to 700 nm have been prepared (Figure 9.2) [45]. The polymeric resin used was doped with a specific fluorescent dye, namely stilbene 420, disodium fluorescein, or rhodamine B, which emit at center wavelengths 420, 535, and 580 nm, respectively. The microfabrication was done in stages. First, the polymeric resin doped with stilbene was used to create a portion of the microstructure by MPL. After development, the polymeric resin doped with disodium fluoride was deposited onto the same substrate. A second part of the structure was fabricated by MPL and then developed again. Finally, the third part of the microstructure was fabricated using the polymeric resin doped with rhodamine. Fluorescence imaging showed that the three parts of the microstructure fluoresced at the different wavelengths, with no apparent evidence of the fluorophores having mixed between the parts. In this process, the order of the stages is interchangeable depending on which part of the microstructure is required to emit at a given wavelength. A fluorescing artificial scaffold with promising applications in cell growth and tracking was fabricated in the hybrid sol-gel photopolymer organically modified silicate (ORMOSIL) doped with rhodamine 6G, fluorescein, LC6500, and coumarin 152 [46]. Biofunctionalization was demonstrated by first immobilizing biotin onto the surface of a microstructure made using an organically modified ceramics (ORMOCER) followed by exposure to fluorescent-dye-labeled avidin [18] or streptavidin [19].

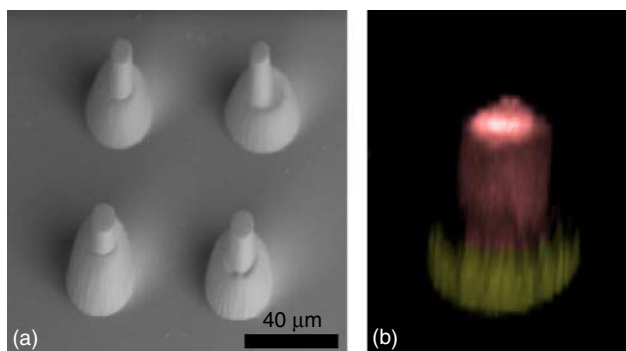


Figure 9.2 (a) Scanning electron microscopy (SEM) image and (b) confocal microscope image of double-doped microstructure. (Otuka 2012 [45]. Reproduced with permission of Optical Society of America.)

9.2.2

Organic Composites for Lasing Microstructures

Organic microlasers (OMLs) have attracted much attention because of their potential for enabling functional devices, particularly lab-on-a-chip systems. The advantages of having a microlaser that uses organic and polymer materials as a gain medium include low cost, compact size, low power consumption, versatility, tunability, and easy integration [46, 49]. However, when using organic components as an active medium, the photochemical processes can become complex because of the potential interplay of absorption and energy transfer between the photoinitiator and chromophore [50]. Additional challenges may include poor solubility of the chromophores in the resin, clustering, self-aggregation, and fluorescence self-quenching at high concentrations [49, 50]. To overcome these problems, and to increase the concentration of the gain medium, a solid-state microcavity was fabricated using a 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyrane (DCM)-doped dendrimer incorporated into a pre-polymer material [50]. The dendrimer was made using repeated ester-branching groups and 64 end groups reacted with acrylic L-phenylalanine and Fmoc-L-phenylalanine. The photopolymerized dendrimer encapsulates the laser dye, providing site isolation which limits intermolecular energy transfer and fluorescence quenching. The DCM-doped dendrimer gain medium concentration reached a maximum of 4.2 wt% compared to only 0.5 wt% without the dendrimer. The microcavity was optically characterized and found to lase at $\lambda = 612$ nm with a spectral bandwidth of 0.15 nm above threshold under an optical excitation intensity of 0.05 μ J per pulse [50]. Using a carbosilane dendrimer and fluorescein as the gain medium, the laser dye doping concentration was increased to 4.95 wt% in the photocured resin [49]. Using MPL, a distributed feedback resonator composed of cuboid arrays with suspended fibers was created. The resonator was observed to have an amplified spontaneous emission at $\lambda = 556$ nm with a threshold of 0.30 μ J per pulse.

A cuboid-shaped OML was fabricated using the 1,3,5,7,8-pentamethyl-2,6-di-*tert*-butylpyrromethen-difluoroborate complex (PM-597) as the gain medium, doped in a SR9020 triacrylate monomer mixed with a photoinitiator without the aid of dendrimer to increase the concentration [51]. The concentration of the OML gain medium was 0.8 wt%. The OMLs were fabricated directly on the glass substrate or on top of a body-centered tetragonal (BCT) woodpile PC pedestal (Figure 9.3). Fabricating the OML atop a PC decoupled the laser from the substrate and reduced the lasing threshold by a factor of 30.

9.2.3

Organic Composites for Electrically Conductive Microstructures

Electrically conductive 3D microstructures have many applications, including ion-exchange media, chemical sensors, organic photovoltaics, MEMS, micro-actuators, and lab-on-a-chip devices. A microstructure was fabricated in a

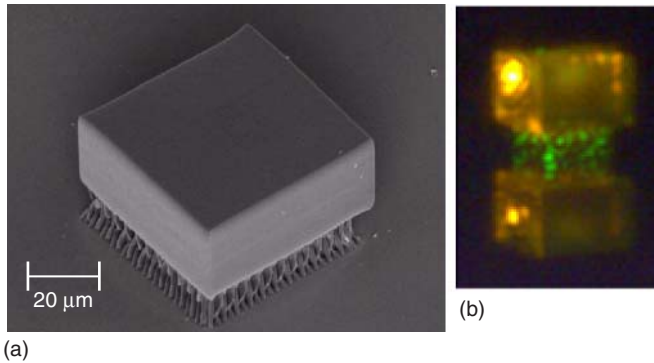


Figure 9.3 (a) SEM image and (b) optical image of an organic micro-laser fabricated on top of a body-centered tetragonal woodpile PC. (Chen 2014 [51]. Reproduced with permission of Optical Society of America.)

polymer composite containing single-wall carbon nanotubes (SWCNTs) at 0.01 wt% via MPL at $\lambda = 800$ nm [52]. Aggregated SWCNTs linearly absorb at 800 nm and compete with the photoinitiator for the absorption of photons. This competition affects the MPL threshold, causing portions of the fabricated structure to shrink and appear distorted. To limit excess absorption, avoid damage to the SWCNTs, and improve structural integrity, the wavelength for MPL was shifted to $\lambda = 780$ nm, which corresponds to a valley between absorption peaks of the SWCNTs while still being suitable for two-photon polymerization. With this adjustment, robust 3D structures, including nanowires with lateral spatial resolutions as low as 200 nm, were fabricated in the composite, and the SWCNTs were observed to be uniformly embedded throughout the structure [52]. The SWCNTs were also found to be partially aligned within the nanowires, and it was suggested that this alignment could be exploited to create devices with improved mechanical and electrical properties.

An electrically conductive all-polymer 3D microstructure was fabricated by MPL and shown to have a conductivity of 0.04 S cm^{-1} (Figure 9.4) [53]. A blend of different amounts of 3,4-ethylenedioxythiophene (EDOT) dissolved in polyethylene glycol diacrylate (PEG-DA) was stirred for 30 min and degassed in a 1×10^{-2} mbar vacuum chamber for 1 h. The free-radical photoinitiator 2-hydroxy-4-(2'-hydroxyethoxy)-2-methyl-propiophenone (5 wt%) was added to different concentrations of the PEG-DA/EDOT blend, syringed through a 0.2-μm pore filter, and degassed for 5 min at 1×10^{-2} mbar. The PEG-DA/EDOT blend was then used to fabricate microstructures by MPL. The free-standing microstructures were subjected to oxidative polymerization in a bath of iron(III)chloride hexahydrate melt, which converted EDOT to poly-3,4-ethylenedioxythiophene (PEDOT) and increased electrical conductivity. The conductivity was found to be

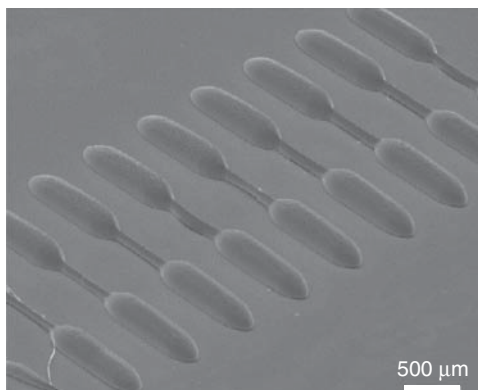


Figure 9.4 SEM image of the all-polymer conductive microstructure fabricated using two-photon polymerization. (Kurselis 2013 [53]. Reproduced with permission of Optical Society of America.)

directly limited by the concentration of the EDOT and reached a maximum of 0.04 S cm^{-1} at 17 vol% EDOT.

9.2.4

Other Optically Active Microstructures

Optically birefringent microstructures with properties that can be altered by external means have direct application in optical data storage, optical switches, and waveguides. A reversibly birefringent microstructure was fabricated by MPL using a composite consisting of a triacrylate resin doped with the azo-aromatic chromophore disperse red 13 (DR13) [54]. A birefringence of 5×10^{-5} was achieved using 1 wt% DR13. The birefringence arises as a result of optical ratcheting of DR13 molecules that occurs under continuous exposure using linearly polarized excitation at $\lambda = 514.5 \text{ nm}$. The birefringence could be induced and later erased by either heating the sample or by exposing it to circularly polarized laser light. As azo-aromatic chromophores have low residual birefringence, microstructures were fabricated using an azo-polymer HEMA-DR13, which was shown to increase the residual birefringence by $\sim 35\%$ [55].

A nonlinear 3D PC was fabricated by MPL using the nonlinear chromophore disperse red 1 (DR1) (Figure 9.5) [7]. DR1 was reacted with (3-isocyanatopropyl) triethoxysilane to form the functionalized silicon alkoxide precursor SGDR1, which was then mixed with methacryloxypropyl trimethosilane (MAPTMS) and the photoinitiator Irgacure 369. This composite was used to fabricate a woodpile PC. The structure did not exhibit a complete photonic bandgap due to the low refractive index contrast of SGDR1 and air, which is roughly 0.5. Fourier transform infrared spectroscopy (FTIR) indicated that a stopband was present in certain directions at infrared wavelengths.

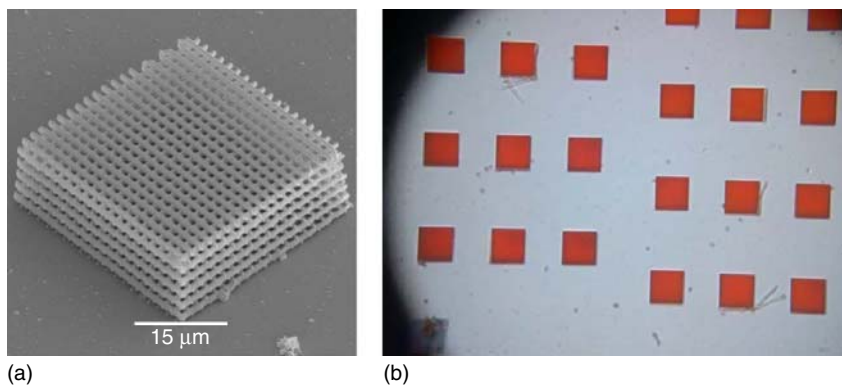


Figure 9.5 (a) SEM image and (b) optical image of the PC made by an active nonlinear chromophore SGDR1:MAPTMS composite. (Farsari 2008 [7]. Reproduced with permission of Springer.)

9.3

Multiphoton Processing of Oxide-Based Materials

Bulk metal oxides can have unique properties that depend sensitively upon their chemical composition and structure. These include large mechanical hardness, large and often tunable refractive index, wide optical bandgap, either high or low electrical resistivity depending upon structure and composition, photomissivity, and ferromagnetism. Reports have shown that some of these properties can be obtained by blending oxides into organic materials, thereby forming composites. Metal oxide nanoparticles are known for their promising electronic properties, which can be exploited for cancer treatment, chemical and biosensing, and photovoltaics [56].

Several approaches have been demonstrated for creating metal oxide microstructures by MPL. Metal oxide nanoparticles have been homogeneously dispersed in polymers, forming photo-patternable composites for MPL [57, 58]. Inorganic–organic hybrid polymers have also been employed, where the inorganic backbone contains the species needed for the targeted metal oxide, and post-MPL processing is used to transform the patterned hybrid into a metal oxide 3D form [59–61]. Metal oxides have been introduced through sol–gel processing [62]. The simplest approach involves MPL using polymer composites containing metal oxide nanoparticles. Ideally, the weight loading of the metal oxide should be as high as possible; however, it is limited because high weight loading can interfere with the MPL process. Additionally, high weight loading increases the viscosity of the resin, making it difficult to mix and process, and possibly also resulting in phase separation [8, 63]. Surface functionalization of metal oxide nanoparticles has been used to suppress phase separation and achieve high weight loading [64]. Creating a metal oxide backbone via sol–gel processing can provide access to structures with specific properties [65–67]. Sol–gel processing is relatively simple and gives the added benefit of mechanical

and chemical stability, although structures made from this process also suffer from shrinkage and distortion. Sol–gel processing has been used extensively for Si–O inorganic–organic hybrids, and is reviewed in detail elsewhere in this volume.

9.3.1

Titanium Dioxide

Titanium dioxide (TiO_2 , titania) has both high refractive index and high transparency at visible wavelengths, which is not available with many other materials. Along with somewhat enhanced robustness, these properties have made composites of TiO_2 very worthwhile to explore. Structures of titania composites have been fabricated by processing complexes of titanium(IV) acrylate or titanium(IV) ethoxide blended with a photopolymer [8]. After fabrication, the nanoparticle composite contained titanium hydroxide as a result of air exposure. The structure was then converted to TiO_2 by annealing to drive off the organic components.

Titanium(IV) *n*-butoxide complexed with benzoylacetone undergoes bond cleavage when irradiated with UV light or by MPL, rendering it insoluble in organic solvents like acetone. The resulting composite contains TiO_2 , which can be annealed, changing the titania morphology and eliminating organic components. This process yields a structure with high refractive index and was used to create the first titania PC having a complete bandgap at visible wavelengths [68].

Three-dimensional structures have been fabricated by MPL using composites based on titania nanoparticles or silicon/titanium sol–gel hybrids. Sol–gel hybrids were created by combining various amounts of titanium(IV) isopropoxide (TIP) and MAPTMS. This approach was used to tune the refractive index by varying the ratio of TIP and MAPTMS in the composite (Figure 9.6) [69, 70]. These and related approaches for creating 3D structures of nearly pure TiO_2 [71, 72] have shown how effective the methods are for creating microscale photonic devices with very high or very specific refractive index.

9.3.2

Zinc Oxide

Zinc oxide (ZnO) is a semiconductor that can give enhanced conductivity, photoemission, or hardness when added to composite structures. In one account, ZnO nanoparticles having an average diameter of 50 nm were added to 1 wt% cinnamate acrylate monomers [73]. Nanoparticles of shapes other than spheres were also used. ZnO nanowires with a length of 1–3 μm were prepared using a hydrothermal technique and directly added to acrylate monomers up to 5 wt% [56, 57]. The composites containing ZnO fluoresced at 570 nm. Other emission/absorption bands were obtained with rod-shaped nanoparticles. Three-dimensional structures based on these composites exhibited enhanced fluorescence at ~ 450 nm [57].

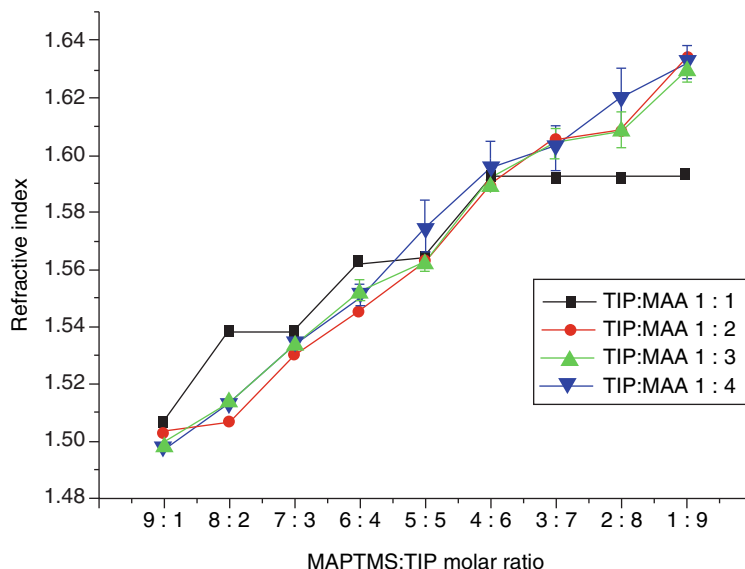


Figure 9.6 Dependence of the refractive index of the content of titanium(IV) isopropoxide (TIP) within sol–gel composites used for MPL. (Sakellari 2010 [69]. Reproduced with permission of Springer.)

9.3.3

Zirconium Dioxide

Zirconium dioxide (ZrO_2) is a hard material with high refractive index, which makes it well suited for composite microstructures. Chichkov and coworkers explored the use of the Zr-containing polymer sol–gel composite SZ2080 for MPL (Figure 9.7) [65, 74–76]. The zirconium oxide increases the hardness and reduces the shrinkage of the material upon processing, which are two common problems associated with fabricating high-resolution 3D structures by MPL. The resolution of this system was improved by formulating composites containing 2-dipentaerythritol pentamethacrylate [61]. This molecule features a large number of reactive acrylate groups, which substantially increases crosslinking and serves to reinforce the material. Minimum feature widths of ~ 100 nm were achieved with the composite [61].

9.3.4

Iron Oxide

Powered MEMS are needed for many applications, such as microfluidics, lab-on-a-chip devices, and clinical diagnostic equipment. However, such devices are difficult to actuate because their small size increases the complexity of power transfer. One viable and cost-effective method for making powered MEMS is to fabricate parts containing the ferromagnetic material iron oxide (Fe_3O_4) and then

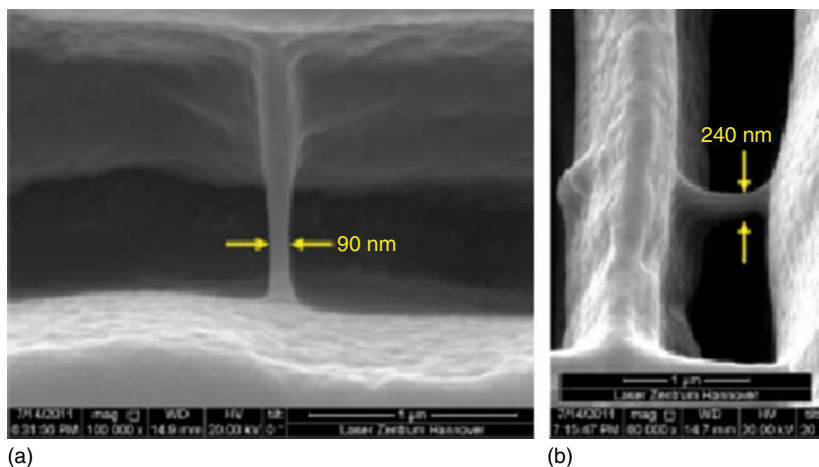


Figure 9.7 (a) SEM image of a feature having an axial dimension of 90 nm created by MPL in a ZrO composite. (b) The same structure observed at an angle of 20°. The minimum height of the structure is 240 nm. (Paz 2012 [61]. Reproduced with permission of Laser Institute of America.)

using magnets to actuate the structures remotely. The magnetic field intensity needed to drive a device can be reduced by using a high weight loading of Fe_3O_4 . Although direct doping of ferric oxide nanoparticles into an organic photoresist has given little success, much higher weight loading has been achieved by modifying the surface of the nanoparticles using organic functionalizing agents. In early reports, the iron oxide nanoparticles were capped with oleic acid to disperse them into an acrylate photoresist up to 2.4 wt% [58]. A similar method was used to coat the surface of cantilevers fabricated in the crosslinkable epoxide SU-8 (MicroChem), which enhanced their sensitivity for detecting volatile molecules [77]. The performance was further improved by chemically modifying the surface of the nanoparticles using 3-(trimethoxysilyl)propyl methacrylate or 6-(methacryloyloxy) hexanoic acid, which stabilized the nanoparticle dispersion toward crosslinking during MPL [78, 79]. The nanoparticle concentration was further increased to 4–5 wt% by functionalizing with 6-(methacryloyloxy)hexanoic acid (Figure 9.8) [64].

9.3.5

Tin Dioxide

Structures of tin dioxide (SnO_2) have properties that are sensitive to the environment and can therefore be used as gas sensors. In one report, a unique metal oxide–organic composite was prepared by mixing and chelating tin(II) dichloride with acetylacetone [80]. The complex is soluble in organic solvents, and forms a gel at high weight loading, but decomposes to an organic-insoluble chelate when exposed to UV light or multiphoton absorption. This material and structures

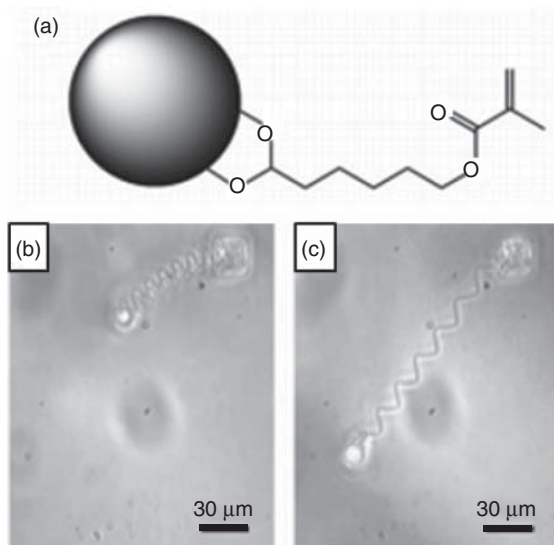


Figure 9.8 (a) Schematic illustration of a Fe_3O_4 magnetic nanoparticle coated with 6-(methacryloyloxy)-hexanoic acid. (b) Optical micrographs of a ferromagnetic micro-spring fabricated by MPL using an iron oxide

nanoparticle composite. (c) The micro-spring was extended while immersed in ethanol by applying a magnetic field. (Tian 2012 [64]. Reproduced with permission of Elsevier.)

created with it by MPL can be calcined to form crystalline SnO_2 . Nanowires of SnO_2 fabricated with this composite exhibited electric resistance that was sensitive to the relative humidity of air (Figure 9.9) [80].

9.3.6

Germanium Dioxide

Like titania, germanium dioxide (GeO_2) is widely used for optics because of its high transparency at near-infrared (NIR) and optical wavelengths. As a result, there is great interest in processes that can be used to create germanium dioxide structures by MPL. This has been achieved by sol processing silicon alkoxides mixed with up to 40 wt% of germanium alkoxide [60]. The refractive index of these composites can be tuned by changing the germanium content, but it was noted that high germanium content compromises the achievable resolution [59].

9.3.7

Silicon Dioxide

There are numerous examples of microstructures fabricated by MPL using composites based on silicon dioxide (SiO_2) nanoparticles and hybrid polymers containing a silicon–oxygen backbone [81, 82]. Silicon oxide nanoparticles blended into composites without any organic modification improves hardness

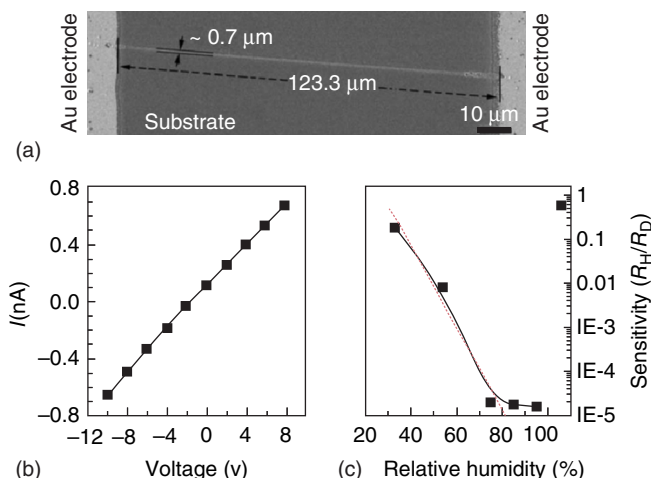


Figure 9.9 (a) SEM image of a SnO₂ nanowire between two gold electrodes. (b) *I*–*V* curve of the SnO₂ nanowire. (c) Dependence of resistance of the SnO₂ nanowire on relative humidity in air. (Guo 2010 [80]. Reproduced with permission of Optical Society of America.)

and reduces shrinkage. A wide range of Si–O hybrid polymers can be created by leveraging the large library of available silane precursors. The precursors are sol–gel-processed, patterned by MPL, and then developed to form silica-containing microstructures. High-refractive-index composites have been created by using phenyl-substituted polymers [66]. High-index siloxane waveguides have been patterned within a cladding of lower index material [83]. A composite based on silanol-terminated polysiloxane and methyl-substituted acryloxysilane has been developed for fabricating optical waveguides by MPL [67]. The commonly used silicon oxide hybrid polymers known as ORMOCERs and ORMOSILs are discussed in detail elsewhere in this volume.

9.4

Multiphoton Processing of Metallic Composites and Materials

Metals can be used to create structures having high electrical and thermal conductivity, high mechanical strength, good optical reflectivity, and other novel properties. Several approaches have been developed for creating metallized structures in conjunction with MPL. These include physical and chemical deposition of metal after MPL, coating functionalized surfaces with metal NPs after fabrication, and direct fabrication of metal-containing structures using composites that include components of the targeted metal. The simplest way to create a metallized 3D structure is to fabricate it by MPL using a conventional polymeric resin and then deposit the targeted metal physically or chemically. This can be achieved through CVD or by physical metal vapor deposition, where the metal is vaporized by resistive heating, electron beam (e-beam) evaporation, or magnetron sputtering (MS).

Electrochemical methods can also be used to deposit metal onto the surface after fabrication. Metal structures can be written directly using photo-patternable composites that contain a source of the target metal, present as metal salts, stabilized nanoparticles, or combinations of the two. These approaches are discussed in greater detail below.

9.4.1

Thermal Evaporation

In thermal evaporation (TE), a metal source is resistively heated under high vacuum and the metal vapor is deposited from a single direction because of the long mean free path of the particles in the deposition chamber [84]. TE is attractive because of its simplicity, but it is limited in that a fabricated structure cannot be conformally coated. Additionally, the heating associated with the process can deform the polymeric microstructure. However, TE can be effective if the fabricated device requires that only the metal is deposited onto a single surface and if suitable conditions can be found that preserve the integrity of the structures. Jia and coworkers fabricated U-shaped split-ring resonators (USRRs) by MPL in the photopolymer AR N 4340, and then metallized the USRRs with a 50-nm gold layer [11]. Any unpolymerized resin, as well as the gold deposited on top of that resin, was then removed using acetone, leaving freestanding structures with a 50-nm gold coating on top. These USRRs were shown to function as optical filters/polarizers in the 2–7 μm wavelength range.

9.4.2

e-Beam Evaporation

e-Beam evaporation is a sputtering technique in which an electron beam is used to deposit metal onto a target under high vacuum [85]. This technique is more complicated than TE, but the issue of high temperatures of the sputtered metal is avoided. Abaddi *et al.* used e-beam evaporation in conjunction with MPL to fabricate a conductive circuit [10]. The structural form of the circuit was created by MPL using the commercial positive-tone photoresist AZ 5214. e-Beam evaporation was then used to deposit a 10-nm-thick layer of titanium, which acted as an adhesion layer, followed by e-beam evaporation of a 100-nm layer of gold, which served as the conductive element of the circuit.

9.4.3

Magnetron Sputtering

MS can generate high-quality films that can outperform other deposition techniques in terms of smoothness and metal grain uniformity [86]. Additionally, as MS involves low vacuum, some conformal deposition can be achieved because the metal vapor collides with other gaseous atoms and molecules during deposition. Previously discussed techniques require high vacuum, so these

collisions are much more infrequent. MS was used by Xiong and coworkers to coat fabricated structures with a 35-nm layer of gold [87, 88]. In this work, various optical functional devices were fabricated using the commercially available MPL photoresist IP-L (Nanoscribe). Polarization-dependent [88] and wavelength-dependent [87] absorbers were fabricated and coated on metals to increase the structures' refractive index contrast, increasing the efficiency of the device (Figure 9.10).

9.4.4

Chemical Vapor Deposition

CVD uses gaseous organometallic precursors to deposit metal onto a structure via a chemical reaction that occurs at the structure's surface [89]. The structure is heated to an elevated temperature, which depends on the organometallic precursor. When the gaseous precursor comes into contact with the heated structure, it decomposes, generating organic fragments that largely diffuse away from the structure leaving behind the residual metal. Because CVD is performed using a comparatively low vacuum, molecular collisions cause metal to deposit conformally on the target surface. However, CVD is slow compared to most other metal coating techniques, sometimes requiring as much as 1 h to deposit 2 nm of the target metal [90]. Additionally, it is not necessarily selective for deposition onto a microstructure versus a supporting substrate or other features on the surface. Wegener's team created functional split-ring resonators (SRRs) by fabricating the forms by MPL in SU-8, coating with a protecting semiconducting oxide layer, and then depositing silver onto the protected structures by CVD using the precursor Ag(hfac)(cod) [90]. Careful control over chamber pressure and temperature, precursor evaporation temperature, and structure temperature yielded a smooth coating of silver metal.

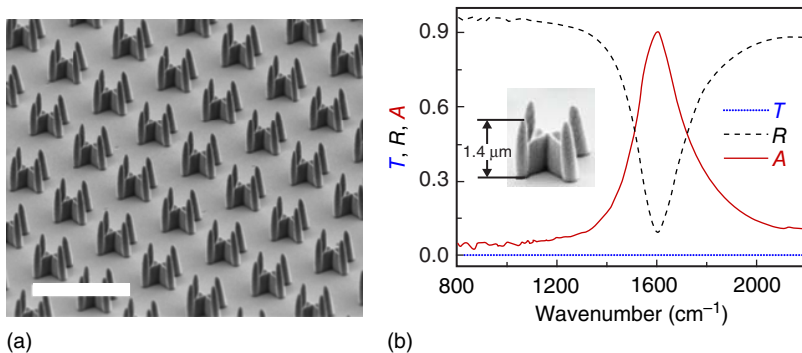


Figure 9.10 (a) SEM image of metal-coated four-tined fish-spear-like resonators (FFRs). The scale bars represent 5 μm. (b) The measured transmission (T), reflection (R), and absorbance (A) for a tine-height of 1.4 μm. (Xiong 2013 [87]. Reproduced with permission of Wiley.)

9.4.5

Functionalization by Attachment of Nanoparticles

Metal NPs synthesized *ex situ* can be chemically bound to a polymeric 3D microstructure created by MPL. Although this technique does not provide complete coverage of the structure, the process can deposit NPs onto all sides of a microstructure, including overhangs. The major advantage of producing NPs separately lies in being able to control the identity of the metal, the NP shape, or the chemical protecting group surrounding the NP. This can allow NPs with specific photonic or binding properties, which can be used in sensing, photonics, or any number of other applications.

Aekbote *et al.* [91] used the Turkevich synthesis [92] to produce citrate-capped Au NPs which were bound to a 3D microstructure to increase their ability to be captured in an optical trap (Figure 9.11). MPL was used to fabricate the 3D structures in SU-8. These were then treated with 3-(aminopropyl)-triethoxysilane to functionalize the microstructure surfaces with amino groups. Immersing the amine-functionalized structures in a low-pH solution protonated the surface and attracted negatively charged citrate-capped Au NPs onto the structures.

Laser-induced transfer (LIT) is another approach for depositing metal NPs onto a surface. In LIT, an amplified laser is focused onto a noble metal surface, causing localized melting and pressure gradients at the focal point. This results in a jet-like structure that ejects molten metal from the area in which the laser is focused. The surface tension of the small droplets causes the metal to form NPs. Reinhardt *et al.* used LIT to coat an organic–inorganic hybrid polymer with Au NPs [93]. First a woodpile PC was created by MPL in an organic–inorganic hybrid polymer. Next, a 50-nm gold film was produced on a separate substrate by MS. The PC was then placed near the gold film, and LIT was used to transfer gold NPs onto the surface. This technique produced Au NPs with a uniform size across the PC surface, although the coating was not conformal.

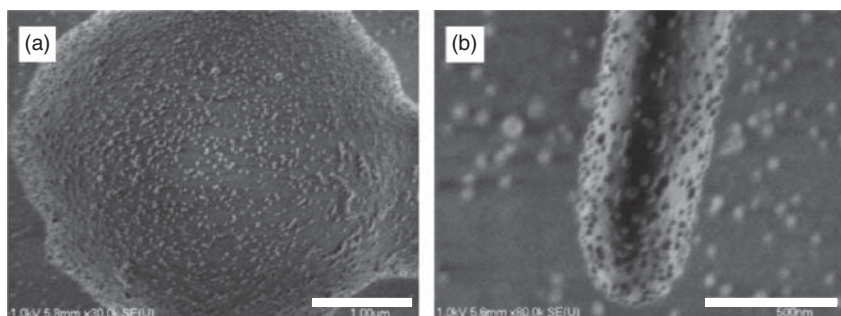


Figure 9.11 Two-photon-polymerized SU-8 microstructures for optical trapping applications. (a) SEM top view image of the spherical and (b) tip areas of the microstructures coated with 24 nm Au NPs. (Aekbote 2012 [91]. Reproduced with permission of Elsevier.)

9.4.6

Electroless Metallization from Solution

Microstructures can be conformally and rapidly coated with metal by electroplating or electroless deposition in solution. Electroplating of polymeric surfaces is inherently difficult because most are not electrically conductive. With electroless metallization (EM), a conductive surface is not required. In EM, a metal ion precursor and a reducing agent are co-present in the solution, along with a stabilizing agent that prevents them from reacting spontaneously. A surface to be metallized is then chemically sensitized and immersed into the EM bath. The sensitizer enables rapid reaction of the metal salt and the reducing agent, forming a conformal coating of metal on the surface. Polymeric surfaces can be sensitized by reaction with SnCl_2 , binding metal NPs, or other means. Both EM and electroless deposition produce metal with a nanoscale morphology that is sensitive to the metal type, the deposition conditions, and additives that can be co-present to control the kinetics of the reaction [12, 94, 95].

The works by Kawata *et al.* [17, 96] and Fourkas *et al.* [13, 97] are among the earliest reports of using EM to deposit metal conformally onto 3D structures created by MPL. A widely used approach for depositing silver onto microstructures involves using a modified Tollens' reagent [98]. This EM bath consists of silver cations dissolved in basic aqueous media and an aldehyde reducing agent. The reducing agent can be a sugar, such as glucose, which exists in solution in an equilibrium between the cyclic form and the aldehyde-terminated open form. Kawata and coworkers fabricated a wide range of microstructures by MPL using a commercial photopolymer, activated their surfaces using SnCl_2 , then deposited silver using a modified Tollens' reagent (Figure 9.12) [96]. They also demonstrated that large-area metallized structures could be created by patterning structures in parallel using a microlens array and then metallizing the structures. Tollens'-like

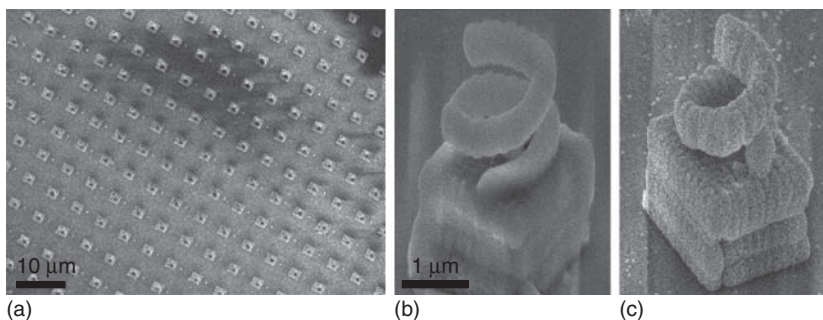


Figure 9.12 (a) SEM image of 3D periodic silver-coated microstructures fabricated on a hydrophobic coated glass surface. (b) Tilted magnified view of an individual uncoated polymer structure composed of a cube (2 μm in size) holding up a spring (height = 2.2 μm ,

inner diameter = 1 μm). (c) SEM image of an individual silver-coated microstructure after electroless metallization. (Formanek 2006 [96]. Reproduced with permission of Optical Society of America.)

approaches have been used to create a wide range of metallized 3D microstructures [95, 99–101].

One of the appeals of EM is that the approach can be selective toward a given surface. Several groups have shown that EM can be used to deposit metal on a polymeric microstructure selectively, leaving the supporting substrate largely metal-free [12, 17, 94, 102]. The selective functionalization was achieved by either copious cleaning or plasma-etching the substrate prior to processing [12, 94, 102], or through chemical modification of the substrate, such as application of a hydrophobic coating prior to casting the photosensitive resin [17].

Selective metallization can be achieved through a two-step process in which a microstructure is fabricated using two different resins, only one of which is active toward EM. Kawata and coworkers fabricated part of a microstructure by MPL using the methacrylate resin KC1102 (JSR), developed to remove unpolymerized material, and then continued fabrication using a composite of KC1102 blended with a methacrylamide, and developed again. The surface of the finished structure was treated with a Tollens'-like reagent. Silver deposited selectively onto those portions of the structure that were fabricated using the methacrylamide-doped resin [103]. Fourkas *et al.* used a similar approach in which parts of a microstructure were fabricated in an acrylate-based resin and others were fabricated using a methacrylate-based resin [13]. After fabrication, the sample was treated with a diamino alkane, which selectively adds to acrylates by Michael addition, and then exposed to a copper EM medium [104]. The metal was deposited selectively at the amine-functionalized surfaces, leaving portions of the structure created from methacrylates un-metallized. This technique was used to fabricate a functional micro-inductor that was electrically characterized (Figure 9.13).

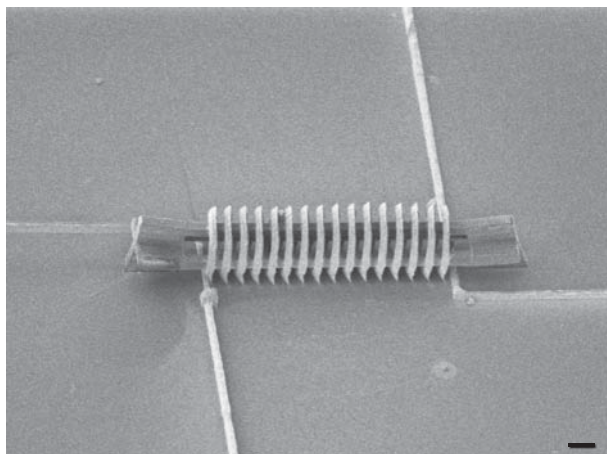


Figure 9.13 SEM image of a copper-coated micro-inductor with a methacrylate support (scale bar corresponds to 10 μm). (Farrer 2006 [13]. Reproduced with permission of American Chemical Society.)

Copper EM has also been used to create movable metallic 3D microstructures [105, 106]. Three-dimensional microstructures were fabricated using an acrylic resin consisting of Sartomer SR-368 and Sartomer SR-499 and functionalized with ethylene diamine. The surface of the amine-functionalized microstructure was sensitized using PdCl_2 . Copper metal was then deposited by EM using 0.6 M Rochelle salt, 0.14 M NaOH, 0.28 M CuSO_4 , and 0.3 M EDTA. The parts of the microstructure attached to the substrate were then laser-ablated, which freed the microstructure from the surface, allowing the microstructure to move. Some microstructures remained attached to the substrate, such as a cantilever [105], while other microstructures were not attached to the substrate but held in place by interconnecting parts, such as a micro-rotor [106].

Kuebler *et al.* used a modification of an EM process first reported by Danscher [107, 108] to deposit electrically conductive and highly reflective silver conformally onto 3D microstructures and woodpile PCs fabricated by MPL in SU-8. The surfaces of polymeric microstructures were activated toward EM by attachment of Au NPs [109, 110]. Silver deposited in this way was shown to have a conductivity of $1 \times 10^4 \Omega^{-1} \text{ cm}^{-1}$, which is 1.5% of that of bulk silver metal [12, 94]. Terzaki and coworkers have compared several approaches for silver deposition and used them to create metallized microstructures created with organic–inorganic hybrid polymers [95].

Kuebler *et al.* fabricated functional metallo-dielectric PCs by using EM to deposit copper onto polymeric lattices created by MPL in SU-8 (Figure 9.14) [102]. Infrared reflectance spectra showed that EM significantly transformed the optical properties of these PCs. Whereas the polymeric PCs exhibited the usual narrow stopband, metallization created a broad “plasmonic” stopband, characterized by high reflectance at all wavelengths below the stopband and low reflectance at wavelengths above the stopband. These metallo-dielectric PCs behaved like “hot mirrors” in which the structure transitions from reflecting to nonreflecting at a wavelength that can be tuned by simply changing the period of the lattice.

Misawa *et al.* fabricated woodpile PCs in SU-8 and coated these structures in nickel [111, 112]. This process involves fabricating a microstructure by MPL in SU-8, sensitizing the surface using aqueous SnCl_2 , activating the surface for EM with aqueous PdCl_2 , and then finally immersing the structure in a nickel EM bath consisting of NiCl_2 , NH_4Cl , NaH_2PO_2 , and NH_4OH at $\text{pH} = 9.2$ at 40°C . The microstructures fabricated using this process were shown to be partially reflective in the infrared. Ren *et al.* used a similar process to create nickel-plated PCs and showed that they behaved like thermal emitters when heated (Figure 9.15) [113]. Wang *et al.* also used a nickel EM process to create ferromagnetic microstructures that could be manipulated using a magnetic field [114]. The metal coating also increased the hardness and modulus of the microstructure by 10- and 9-fold, respectively.

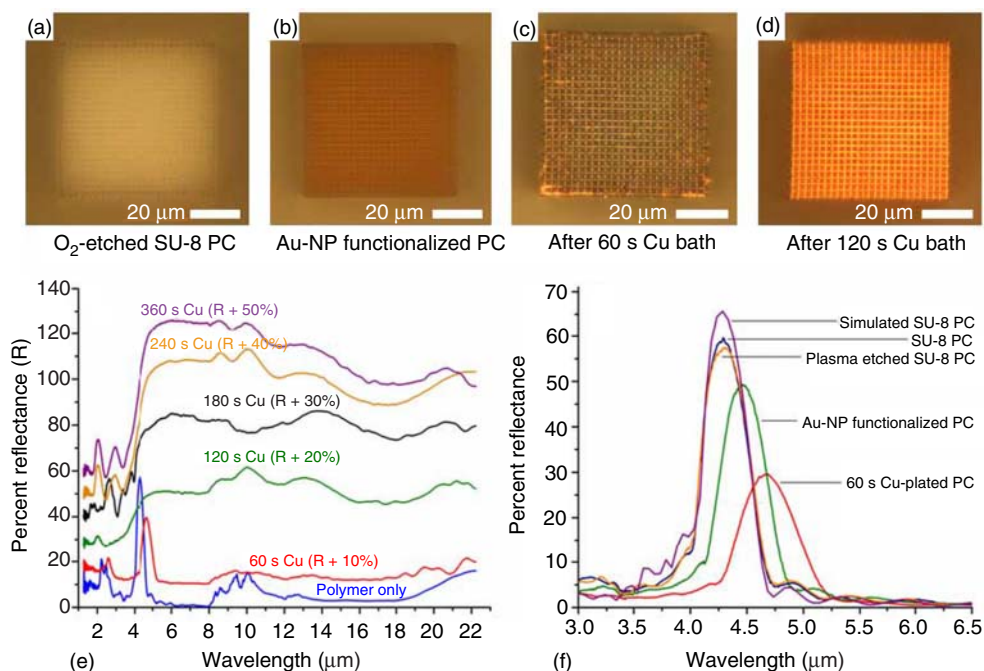


Figure 9.14 (a–d) Optical reflection image of SU-8 PCs at various stages of the copper deposition process. (e,f) FTIR reflection spectra of PCs at various stages of copper

deposition. Each spectrum in (e) is offset vertically by 10% for clarity. (Tal 2007 [102]. Reproduced with permission of Optical Society of America.)

9.4.7

Multiphoton Lithography of Nanoparticles Supported in a Polymer Matrix

Metallized 3D microstructures can also be prepared by incorporating metal ions in the photopolymer used to create the structure. This approach can yield structures with metal distributed throughout the interior of the 3D microstructure, rather than merely on the surface. This can be advantageous for certain applications and, in principle, could simplify the fabrication process, insofar as the metallized structure can be produced in a single MPL step.

Shukla *et al.* introduced a method for creating Au NP-containing SU-8 microstructures for various photonic applications [115, 116]. In their approach, HAuCl₄ and the two-photon-absorbing dye AF 380 were blended with SU-8. AF 380 was included as a photo-activatable reducing agent that could transfer electrons to Au³⁺ cations upon photoexcitation, leading to the formation of Au NPs. After MPL, the microstructures were developed as usual. Figure 9.16a shows lines fabricated on a glass substrate under different exposure conditions. The line widths did not change with varying scan speed, but the number density of Au NPs was found to increase with exposure. Microstructures fabricated in the

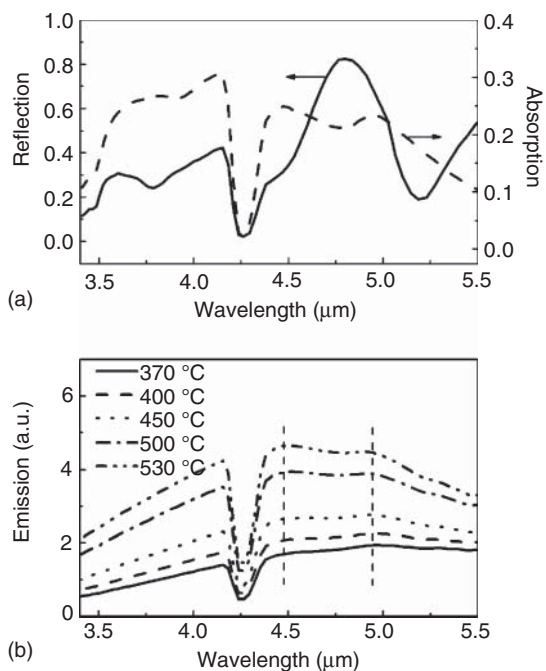


Figure 9.15 (a) Infrared reflection (solid line) and absorption (dashed line) of metallized PCs. (b) Thermal emission spectra of the PCs as a function of temperature. (Ren 2013 [113]. Reproduced with permission of Royal Society of Chemistry.)

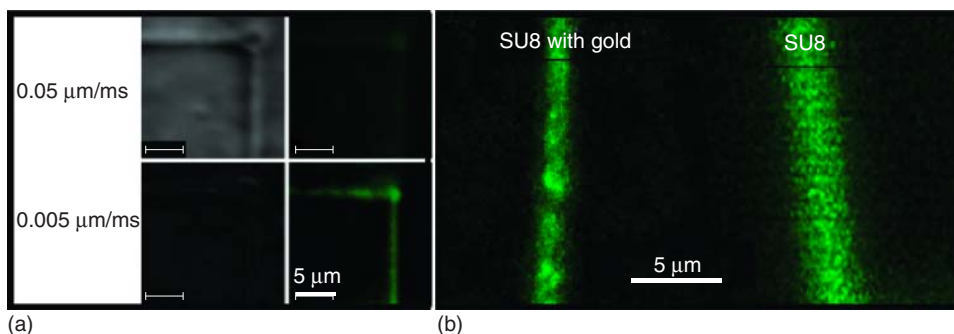


Figure 9.16 (a) Confocal transmission (left) and fluorescence (right) images of lines produced at scanning speeds of 50 $\mu\text{m s}^{-1}$ (top) or 5 $\mu\text{m s}^{-1}$ (bottom) at 10 mW. (b) Confocal images of gold precursor-doped SU-8 line

and undoped polymeric feature at the same power (40 mW) and scan speed (50 $\mu\text{m s}^{-1}$). (Shukla 2011 [116]. Reproduced with permission of American Chemical Society.)

presence of the gold precursor had smaller line widths than those fabricated with neat SU-8 (Figure 9.16b). The fabricated lines were conductive to within an order of magnitude of bulk gold due to the high loading fraction of the gold precursor. Microstructures with metal NPs have been fabricated in several other materials, including Ag NPs in poly(vinylpyrrolidone) [117], Ag NPs in SU-8 [118], Ag NPs in a porous SiO₂ framework [62], Au NPs in an acrylate matrix [119], and Au, Cu, and Ag NPs in borosilicate glass [56].

Tanaka *et al.* took advantage of the fact that Au³⁺ quenches the fluorescence of rhodamine B dye, whereas Au NPs do not, to develop a direct-write medium for 3D optical data storage [120]. The investigators doped poly(methylmethacrylate) matrix (PMMA) with rhodamine B and HAuCl₄. Exposing the composite to focused femtosecond laser pulses locally excited the rhodamine B, leading to photo-induced reduction of Au³⁺ and formation of Au NPs. In regions where Au NPs were created, fluorescence was restored. Data could be stored digitally by writing Au NP-rich pixels within the volume of the material and reading out the data by laser-induced fluorescence. This system is useful for write-once–read-many (WORM) applications, like long-term data storage.

9.4.8

Direct Writing of Continuous-Metal Microstructures

When the goal is to create microstructures of *continuous* metal, then directly writing metallic features would appear to be the preferred route. However, this approach is not straightforward, because most chemical systems for forming metal in solution or viscous media tend to generate poly-nucleated and/or discontinuous NPs, rather than the bulk metal. The first report of direct fabrication of metallized structures was presented by Stellacci *et al.* [9]. In their approach, a composite was formulated of poly(vinylcarbazole) (PVK), Ag NPs, AgBF₄, and a two-photon-excitable dye that could be spin-coated onto surfaces. Laser excitation of the dye activated electron transfer to the Ag⁺ ions, which caused Ag NPs to grow further and fuse into continuous metal within the PVK matrix. The host polymer could then be dissolved using dichloromethane, leaving a freestanding metallic nanostructure. Maruo *et al.* also used a host matrix as a support to directly write silver lines and pyramids in a PVP matrix containing silver nitrate [121]. Metal–organic frameworks (MOFs) have also been used as a host matrix by Ameloot *et al.* to write micro-QR codes and microcircuits [122].

Although it is generally advantageous to use a host matrix, this may not always be possible. Directly preparing metal microstructures from a liquid solution provides easier processing, but also pose new challenges in that NPs or other metal generated by MPL within a solution medium may not have a firm point of attachment on the substrate or other portions of the microstructure. Ishikawa *et al.* addressed this issue by scanning the focused laser at a slower rate and focusing at the surface of previously deposited metal [123]. This approach caused newly created NPs to aggregate, sinter, and become fused with the underlying layer (Figure 9.17). Lu *et al.* developed a medium for MPL of continuous gold

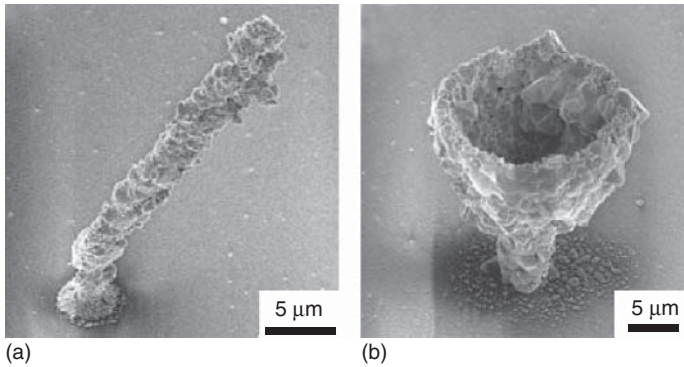


Figure 9.17 SEM images of a freestanding (a) silver tilted rod and (b) silver cup on a substrate. The length of the rod and the angle relative to the substrate are 35 μm and 60°, respectively. The height and the top and bottom diameters of the cup are 26, 20, and 5 μm , respectively. (Ishikawa 2006 [123]. Reproduced with permission of American Institute of Physics.)

metal based on Au^{3+} and an ionic liquid. The ionic liquid helped the formation of gold NPs upon laser irradiation and encouraged their aggregation into continuous gold metal features [124].

Fourkas *et al.* reported a hybrid two-step approach for creating continuous metal features [97, 125]. First, silver nitrate/PVP solutions were spin-coated onto substrates forming films. Then MPL was used to photo-reduce Ag^+ in the PVP films, forming silver lines [125]. This process could also be carried out on the surface of microstructures fabricated earlier by MPL using a metal-free photopolymer [97]. The silver lines were then enhanced with by copper EM, forming a microstructure with highly selective and conductive metallization.

9.4.9

Metal Backfilling by Electroplating

As mentioned previously, it is inherently difficult to electroplate polymeric microstructures because of their lack of conductivity. However, Gansel *et al.* have found a way to use electroplating to backfill a micro-patterned polymeric film with gold [23]. The positive-tone resist AZ 9260 (MicroChemicals GmbH) was used to create helical voids on top of an indium-tin oxide (ITO) substrate, which served as the cathode. After MPL and development, a platinized tin mesh was placed on top of the polymer block, to serve as an anode. The two-electrode sample was placed in a solution of sodium disulfiteaurate(I), sodium sulfite, ethylenediamine for stabilization, and disodium ethylenediamine tetraacetic acid. The solution was held at constant temperature while a fixed potential was applied at constant current to reduce Au^+ to gold metal at the ITO electrode. This resulted in the growth of continuous bulk metal within the helical holes of the patterned polymer film. Plasma etching was then used to remove the polymer

matrix, leaving behind a structure of freely standing individual gold helices. These structures were shown to selectively reflect circularly polarized light of one handedness and transmit the other.

9.5

Multiphoton Processing of Semiconductor Composites and Materials

Semiconductor devices are important for electronic, optical, and sensing applications. Significant strides have been achieved in extending MPL for patterning semiconductors through the development of specialized photo-patternable chalcogenides, polymer composites that contain semiconductor NPs or their chemical precursors, and post-patterning processes, such as ALD. Understandably, many investigations have focused on demonstrating new material processes by creating functional 3D PCs, waveguides, or other optical devices, for which semiconductor materials are often best suited.

9.5.1

Structures Functionalized with Nanoparticles

The most commonly employed NPs consist of lead sulfide, lead selenide, or cadmium sulfide. Core/shell compositions are commonly used because the radiative properties of core-only NPs can be adversely affected by oxidation, contamination, and photobleaching [126]. By having a shell of a wider bandgap semiconductor, the quantum yield of the emitter is increased and stability is improved. Semiconductor NPs can have high quantum efficiency and narrow, tunable emission lines, which makes them well suited for micro and nanophotonic devices [127]. NPs can also be used to engineer linear or nonlinear optical properties and to increase quantum efficiency in certain wavelength ranges. The refractive index, absorption and emission wavelengths, and stop gaps of the hybrid material structure can be tuned via the composition and structure of the NPs. Fabrication parameters of the PCs and size distribution of the NPs can be altered to obtain targeted embedded NP emission wavelengths at or near the bandedge of the PCs [128]. NP-based microstructures can be formed by depositing the NPs onto a polymeric structure created by MPL, or performing MPL using a composite that contains the NPs or an NP precursor.

9.5.2

Structures Functionalized using NP–Polymer Composites

Free-standing 3D microstructures containing semiconductor NPs have been fabricated by MPL using polymeric photoresists that are preloaded with semiconductor NPs or by dispersing the NPs into a resin using the sol–gel method [127–130]. PbS and PbSe NPs have been used because of their NIR emission band, large Bohr radius, and high third-order nonlinearity [127]. After photo-patterning, the

unpolymerized material could be washed away, leaving the 3D nanocomposite structure [131].

Li *et al.* fabricated 3D woodpile PCs with a photonic bandgap in the NIR using a commercial PbSe NP-doped composite material (1550 nm PbSe Evicomposite); however, aggregation during the fabrication process was observed to contribute to structure defects [128, 131]. Three-dimensional woodpile PCs with stopbands of 80% suppression in transmission in the telecommunications wavelength region were created by Jia *et al.* using the hybrid organic–inorganic resin ORMOCER containing PbS NPs [127, 129, 130]. The NPs were found to be evenly dispersed in the resin, and Z-scan measurements confirmed high third-order nonlinearity of the polymerized nanocomposite film [127, 129, 130]. The stopbands red-shifted with increasing NP concentration as a result of the increase of effective refractive index. At both low and high concentrations, the nanocomposites were transparent at visible wavelengths [127, 129, 130]. Venture *et al.* synthesized PbS NPs and had their surface chemistry modified in order to reduce aggregation before dispersing into the commercial photopolymer NOA63 [132]. The investigators were able to control the size of the NPs by varying either Pb:S ratio or the reaction time. PbS NPs were treated with 3-mercaptopropyl-trimethoxysilane followed by ultrasonication in order to overcome NP aggregation before dispersal in NOA63, and the resulting NP nanocomposites showed an increased refractive index. PCs made in the composite material containing modified PbS NPs in NOA63 were observed to have stopbands at telecommunication wavelengths.

9.5.3

Structures Functionalized by In Situ NP Formation

NP-containing microstructures can be created by MPL in a liquid composite that contains chemical precursors of the NPs [21, 133, 134]. As the focused laser beam is scanned within the composite, it both forms the polymeric matrix of the microstructure and induces chemical formation of NPs. After laser patterning, the unpolymerized material can be washed away, leaving the 3D nanocomposite polymer structure.

Sun *et al.* fabricated 3D log-pile PCs using a composite that formed CdS NPs *in situ* during MPL (Figure 9.18) [21]. The composite consisted of acrylate monomers, oligomers, a photoinitiator, and cadmium methacrylate [21, 134]. After MPL, the microfabricated structures were treated with hydrogen sulfide gas to form the CdS NPs [21, 134]. Nanocomposites with tunable fluorescence maxima were created by controlling the amount of crosslinker in the resin [134].

Gan *et al.* used PbSe–NP composites to create narrow-bandgap PCs [133]. The PbSe precursors lead oleate (PbOA) and TOPSe (Se dissolved in trioctylphosphine) were dissolved in 1-octadecene (ODE) and then blended with a photopolymer. The high solubility of the chemical precursors in the organic solution allowed laser beam-induced formation of structures containing a high loading of sufficient amounts of Pb and Se elements. Three-dimensional PbSe structures consisting of overlaying lines with sub-micrometer widths of 500 nm were fabricated using this

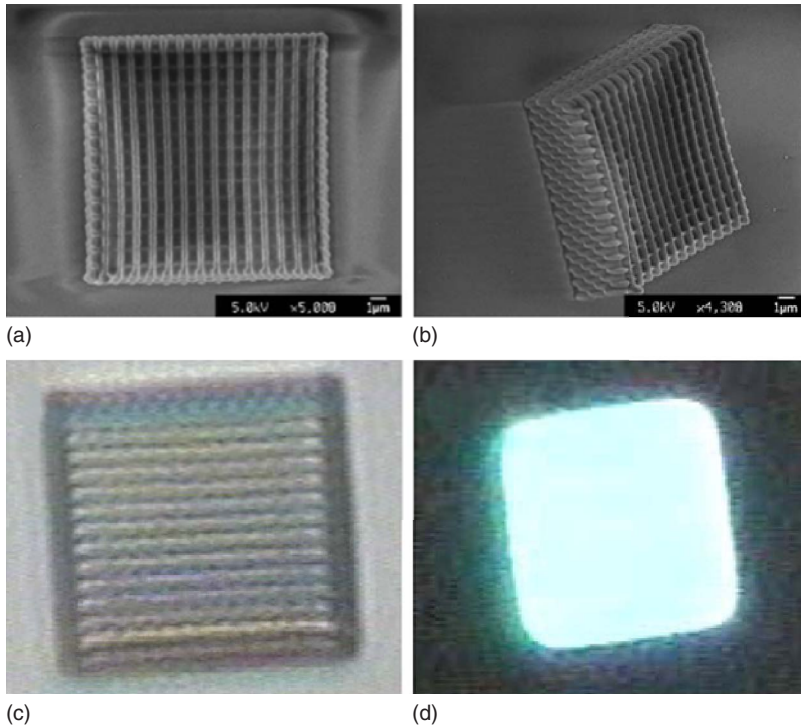


Figure 9.18 Top (a) and side (b) view SEM images of 20- μm -wide 3D PCs formed in a CdS NP-polymer nanocomposite. (c) Optical and (d) fluorescence microscopy images of the PCs. (Sun 2007 [21]. Reproduced with permission of Springer.)

composite. Energy-dispersive spectrum (EDS) measurements of the fabricated structure confirmed the formation of the PbSe [133].

9.5.4

Structures Functionalized by NP Coating

Semiconductor NPs can also be integrated into microstructures by first fabricating them by MPL in a photopolymer and then chemically functionalizing the microstructure surface with the NPs [12, 135]. Three-dimensional woodpile PCs with a bandgap centered at a wavelength of $2.04\mu\text{m}$ were fabricated using an ORMOCER and then infiltrated with PbSe NPs for the first time by Li *et al.* [128, 135]. PbSe NPs were prepared by the method described by Yu *et al.* [136] and had a quantum efficiency of more than 85% [135]. The NPs were dissolved in a chloroform or toluene solution, and then drop-casted onto the PC, which dispersed them evenly throughout the structure. The stopband of the PC was observed to increase with concentration of NPs in the solution because of the increased fill factor and refractive index. The emission spectrum of the structure exhibited redistributed spontaneous emission [135]. Three-dimensional woodpile PCs with planar defects

were fabricated in an ORMOCER and coated with PbSe/CdSe core-shell NPs [137]. A molecular linking method was used to ensure that the NPs were attached to the PC surface (Figure 9.19). The polymerized ORMOCER structure was functionalized with an amino group prior to immersing in the NP solution to obtain multiple layers. The emission peak overlapped with the stop gap of the PC, which enhanced the spontaneous emission.

Buso *et al.* demonstrated an effective method for tuning the refractive index of ORMOCER 3D woodpile PCs coated with CdS NPs [138]. The PC surface was first pretreated with 3-aminopropyl-triethoxysilane solution in toluene to ensure NP attachment [138]. Then, CdS NPs were deposited using a modified chemical bath deposition (CBD) approach. As the thickness of CdS layers deposited onto the PC lattice increased, the stopband increased in amplitude and shifted to longer wavelength by as much as 375 nm. The shift in the stopband was attributed to an

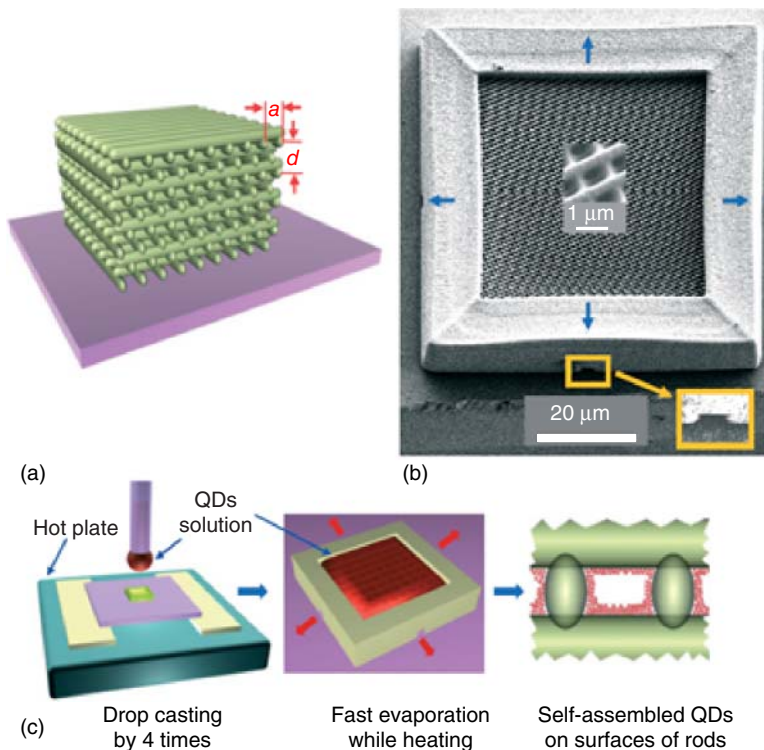


Figure 9.19 (a) Schematic of a 3D woodpile PC fabricated on a cover glass. For the face-centered cubic (fcc) symmetry, the lattice period a and the height of every four layers d , satisfy $d/a = 2$. (b) SEM image of a 3D woodpile PC with a 10-μm-wide frame. An

enlarged view is superposed at the center of the image. A square through-hole was fabricated within each side of the frame (noted by arrows). (c) Schematic of the infiltration process. (Li 2007 [135]. Reproduced with permission of Wiley.)

increase in both the rod thickness and the effective refractive index, whereas the increase in amplitude was attributed to the increase in effective refractive index.

9.5.5

Structures Functionalized by Silicon Inversion

Silicon has a high refractive index ($n = 3.45$) and is optically transparent in the infrared, which makes it a good material for creating PCs. But techniques for microfabrication using Si are time consuming and expensive, requiring costly photolithography masks, and multistep procedures [139]. Some of these limitations were overcome by the introduction of the Si double-inversion (SDI) technique, which was reported in 2006 by Tétreault *et al.* and used to create a Si replica of a polymeric PC (Figure 9.20) [15]. PC templates were first fabricated by MPL using a photo-polymer, and then infiltrated with silica (SiO_2) via ALD. The polymeric lattice was removed by plasma etching or calcination in air to reveal the SiO_2 inverse lattice. If needed, the SiO_2 inverse structure was re-infiltrated with additional SiO_2 by ALD to fine-tune the size of the rods comprising the PC. Next, low-pressure CVD was used to deposit Si within the SiO_2 lattice. Hydrofluoric acid was then used to remove the SiO_2 , leaving behind a doubly inverted lattice of Si that was a replica of the original polymeric PC, but now in a material with much higher refractive index. Using this approach, a Si PC was created having a complete photonic bandgap of 8.6%. A similar method was followed by Gratson *et al.* to create hollow woodpile PCs (Figure 9.21) [139].

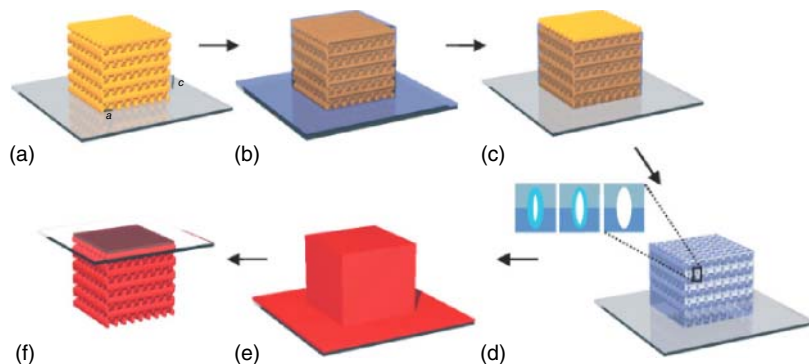


Figure 9.20 Schematic representation of the silicon double inversion (SDI) method. (a) An SU-8 PC template is fabricated by MPL using a photopolymer. (b) The structure is then fully infiltrated with SiO_2 through ALD. (c) Anisotropic reactive ion etching is used to remove the top SiO_2 layer, exposing the SU-8 interior. (d) O_2 plasma etching or calcination in air is then used to remove the SU-8 layer, leaving a SiO_2 inverse woodpile; inset: re-infiltration of the SiO_2 inverse woodpile

by SiO_2 ALD to fine-tune the rod-filling fraction. (e) Low-pressure CVD was then used to re-infiltrate the SiO_2 lattice with Si. (f) The structure was attached to a HF-resistant substrate with a polymer adhesive and the SiO_2 inverse lattice was removed by chemical etching in aqueous hydrofluoric acid (HF), leaving the double-inverted Si woodpile replica. (Tétreault 2006 [15]. Reproduced with permission of Wiley.)

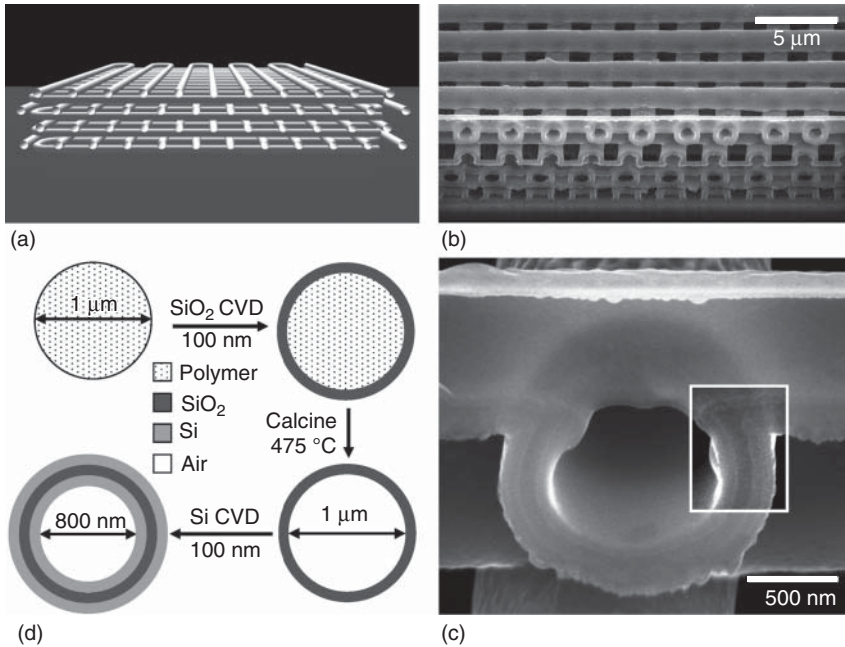


Figure 9.21 (a) Schematic illustration of a hollow-woodpile structure. (b) Low and (c) high magnification SEM images of a Si/SiO₂/Si hollow woodpile structure after focused ion beam milling (eight-layer structure, $d = 2.8 \mu\text{m}$). The contrast-enhanced

inset in (c) reveals the internal structures of the trilayer tube wall. (d) Process sequence for templated assembly of such structures. (Gratson 2006 [139]. Reproduced with permission of Wiley.)

Hermatschweiler *et al.* introduced a modification of the SDI procedure in which a single inversion was used to create a Si inverse PC lattice [22]. In this method, a polymeric PC template was created by MPL and then conformally coated with a thin layer of SiO₂ by ALD. Next CVD was used to completely infiltrate the lattice forming a PC in Si, which was an inverse of the original polymeric template. By applying a thin coating of silica, the aspect ratios of the elliptical woodpile rods and volume fill fraction of the final Si structure were improved and the thin coating provided sufficient stability for the high-temperature Si CVD process. Using this approach, the team fabricated high-quality woodpile Si structures with gap/midgap ratios of 14.2% centered at a wavelength of 2.5 μm.

Stauda *et al.* created 3D Si woodpile PCs with a complete photonic bandgap (PBG) in the telecommunication window by the SDI method using the photoresist IP-L (Nanoscribe) [140]. An additional step of tempering the Si woodpiles at 600 °C was introduced. This transformed the amorphous Si generated by CVD into polycrystalline Si, which possessed a lower refractive index (shifting the bandgap to shorter wavelengths) and lower absorption coefficient. Si woodpiles

with embedded acceptor-type waveguide arrays were optically characterized, and reflectance measurements showed the presence of a broad stopband.

9.5.6

Functional Structures Fabricated in Bulk Chalcogenide Glasses

MPL using chalcogenide glasses (ChGs) has been explored as a means for creating functional nanophotonic devices, without the need for multistep post-fabrication chemical processing. ChGs have a high nonlinearity and a wide IR transmission window with direct application in sensors, photonic waveguides, acoustooptics, and IR optics [141]. Arsenic trisulfide (As_2S_3) is a common ChG chosen because of its transparency in the IR (620 nm to 11 μm) and potential for optical applications [142]. Waveguide structures [143] and gratings [142] have been written in bulk- and fiber-form As_2S_3 . Raman spectroscopy revealed that light exposure breaks As–S bonds and forms As–As homopolar bonds, increasing in the disorder of the glass [143].

McMillen *et al.* and Ródenas *et al.* created waveguides by MPL in bulk GaLaS (GLS) and $75\text{GeS}_2 - 15\text{Ga}_2\text{S}_3 - 4\text{CsI} - 2\text{Sb}_2\text{S}_3 - 4\text{SnS}$ (GCIS) [141, 144]. GLS and GCIS were chosen because of their high transmission in the mid-infrared. GLS was chosen in particular for its high nonlinear figure of merit (FOM) and superior environmental stability [141]. A single-mode buried waveguide was written in GLS and GCIS for use at $\lambda \leq 11 \mu\text{m}$ [144]. Spectral beam shaping and temporal pulse-width tuning were employed to optimize the optical properties of the waveguides [141].

9.5.7

Structures Fabricated in ChG Film

Certain ChGs can be thermally deposited as thin glassy films (200 nm to 20 μm) of photosensitive molecular clusters. As_2S_3 is an attractive material because it has high transparency in the IR, high refractive index ($n = 2.45 - 2.53$), and a low-energy band edge (530 nm), which makes it a good candidate for applications in sensing, waveguiding, and acoustooptics [4, 5]. Raman spectroscopy has been used to show that thermally deposited As_2S_3 is highly photosensitive when it contains a high fraction of As_4S_6 and clusters [4]. Light exposure crosslinks the material, transforming the As_4S_6 cages and other clusters back to As_2S_3 network glass, red-shifting the band edge, and increasing the local refractive index [145]. MPL can be used to photo-pattern thin films of thermally deposited As_2S_3 , and then a chemical etchant can be used to remove the unexposed, non-cross-linked regions. Thermally deposited As_2S_3 can be thought of as an inorganic analog of a negative-tone photopolymer. ChGs have the advantage over photopolymers that they do not exhibit swelling or shrinking during the etching process [146]. The shape, size, and optical properties of features produced by MPL in deposited As_2S_3 films have been shown to be sensitive to the conditions used for thermal deposition, photo-exposure, and etching [4, 5, 145, 147–153].

Single-channel waveguides were fabricated in As_2S_3 thin films by Zoubir *et al.* [145]. Von Freymann *et al.* fabricated functional 3D PCs in As_2S_3 [146]. Three-dimensional woodpile PCs with a complete PBG were fabricated in As_2S_3 and etched using increasing concentrations of diisopentylamine (DIPA) in dimethylsulfoxide (DMSO) [4]. Higher etch selectivity was obtained by using etchants based on novel hindered amines, such as *N*-(4-methoxybenzyl)-(pyren-1-yl)amine. This system produced features as small as 180 nm (Figure 9.22) [149]. Nicoletti *et al.* developed high-quality 3D PhCs with large multi-order NIR stopgaps fabricated in thick (20 μm) As_2S_3 films using multistep DIPA in DMSO etching solutions [154].

Thermal deposition conditions were observed to influence the morphology, size, and appearance of nanostructures in thin As_2S_3 films. Schwarz *et al.* demonstrated that fabricated structures with low deposition rates yielded high etch selectivity, whereas high deposition rates yielded low etch selectivity [5]. Nicoletti *et al.* used a multiple-line scanning method to help reduce the effects of focal spot elongation that result from refractive index mismatch when writing in As_2S_3 [150]. This approach was used to create high-quality PCs with wide-angle stopbands. ChGs were also found to be sensitive to the repetition rate of the laser beam [151]. By investigating the heat accumulation at the laser focal spot and the material's response, an optimal condition for high-resolution fabrication in As_2S_3 was found [151]. Using these MPL conditions, nanorods with dimensions of 68 nm

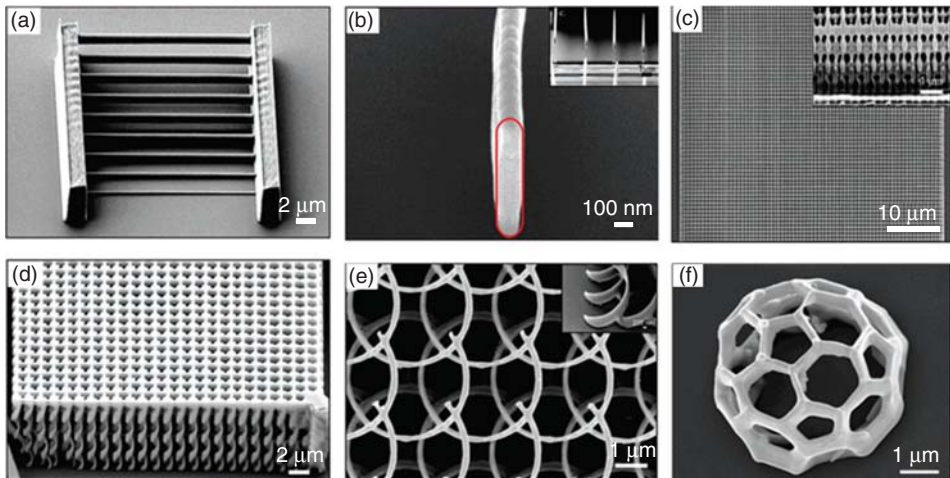


Figure 9.22 Three-dimensional As_2S_3 microstructures created by MPL and chemical etching. (a) SEM image of a “stepladder” test structure. (b) Close-up view of the cross section of (a), demonstrating that the smallest feature size that is definable using this system is on the order of 180 nm. (c) 3D woodpile PC with a lattice constant of

700 nm. The inset shows a cross section created by ion milling. (d) 3D array of spirals. (e) Top view of a 3D array of spirals with individual feature sizes on the order of 180 nm. (f) Close-up of a micro-bucky ball. (Wong 2007 [149]. Reproduced with permission of American Chemical Society.)

($\lambda/12$) and good mechanical properties could be created as well as 3D woodpile PCs with a stopgap in the NIR [151]. Cumming *et al.* used a spatial light modulator to remove spherical aberration, which was found to decrease the size of written features with fabrication depth. This system was used to create high-quality PCs and chiral gyroid PCs in lithium niobate and As_2S_3 films [155, 156].

9.5.8

Structures Fabricated in ChG–NP Composites

As_2S_3 was doped with erbium (Er) to fabricate microstructures that possess both high refractive index and room-temperature photoluminescence (PL). Er provides PL at $1.5\ \mu\text{m}$. Utilizing the gas-phase direct doping (GPDD) technique, Er can be co-evaporated with As_2S_3 forming Er-doped As_2S_3 thin films. Wong *et al.* fabricated high-quality 3D PCs via MPL in the Er/ As_2S_3 photoresist with minimum features sizes of 180 nm and PL at $1.5\ \mu\text{m}$ [147, 148]. Preliminary studies by Nicoletti *et al.* suggest that PCs fabricated in As_2S_3 can be functionalized by coating with PbSe/CdSe core–shell NPs [153]. Diaminoheptane was used to create a self-assembled monolayer of functional ligands, which act as selective linkers so that NPs can be added to the ChG PC in a continuous surface layer. The lattice constant of the PC was chosen to overlap with the NIR emission of the NPs to control their spontaneous emission [153].

9.6

Conclusion

The growing need for functional microstructured materials and devices has driven the rapid development of new processes for MPL. Three-dimensional microfabrication using photopolymers has led to exciting developments and applications. Yet conventional photopolymers alone cannot provide many of the physical and chemical properties that are essential for existing applications, let alone future needs. Other materials are required to create microstructures having low electrical resistivity, high mechanical toughness, high refractive index, optoelectronic function, or resilience under extreme temperature, to give but a few examples. This has led investigators to develop innovative photopolymer composites or nonpolymeric photo-responsive media that can be used to directly create structures with the required properties. Creative and complementary methods of post-MPL processing have also been reported – including surface functionalization, templated deposition, and backfilling – which can be used to direct one or more materials with the desired properties into a targeted microscale form defined by MPL using typical photopolymers.

More such developments can be expected as the technology of MPL matures and as interest in its use grows, particularly for industrial manufacturing. Areas for fruitful exploration include developing methods for patterning multifunctional materials, “smart” materials that actively respond to external stimuli, and

active-form materials that cause the shape of the microstructure itself to change in response to environmental conditions. The existing and emerging material systems for MPL can be expected to form the foundation for dramatic advances in the fields of micro and nanophotonics, opto-fluidics, MEMS, optomechanical systems, sensors, and biomedical devices.

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